

TOPIC 19 – REDOX

19.1 – STANDARD ELECTRODE POTENTIALS

IB Chemistry
T09D04



19.1 – Standard Electrode Potentials

- 19.1.1 Describe the standard hydrogen electrode. (2)
- 19.1.2 Define the term standard electrode potential, E^\ominus . (1)
- 19.1.3 Calculate cell potentials using standard electrode potentials. (2)
- 19.1.4 Predict whether a reaction will be spontaneous using standard electrode potential values. (3)



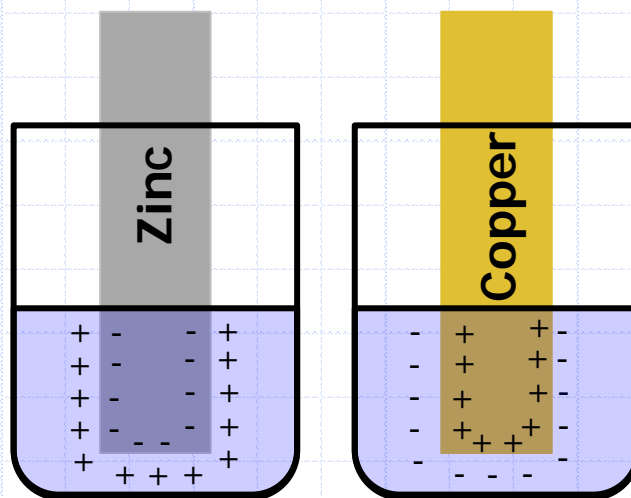
19.1

Standard Hydrogen Electrode

19.1.1 Describe the standard hydrogen electrode. (2)

- A chemical equilibrium is known as **redox equilibrium** and is established when a metal is left in an aqueous solution of it's ions
 - Forward (M-ions enter solution) $M(s) \rightarrow M^{n+}(aq) + ne^{-}$
 - Reverse (deposit on metal) $M^{n+}(aq) + ne^{-} \rightarrow M(s)$
 - Equilibrium $M(s) \rightleftharpoons M^{n+}(aq) + ne^{-}$

Since Zinc is reactive:
 $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^{-}$
*Lies to the **RIGHT***



Since Copper is unreactive:
 $Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^{-}$
*Lies to the **LEFT***



Solutions with $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$ ions respectively

Types of Half Cells

■ There are three (3) types of half cells

- Metal immersed in its own ions
- Inert Electrode (graphite, platinum, etc) immersed in an aqueous solution containing two ions of the same element (ex, $\text{Fe}^{2+}/\text{Fe}^{3+}$)
- Gas bubbling over an inert electrode in an aqueous solution of ions of that gas (standard hydrogen electrode)

■ Put together any two half cells and

- Electrons will flow from reducing agent → oxidizing agent
- Most reactive will be oxidized (reducing agent)
- Least reactive will be reduced (oxidizing agent)



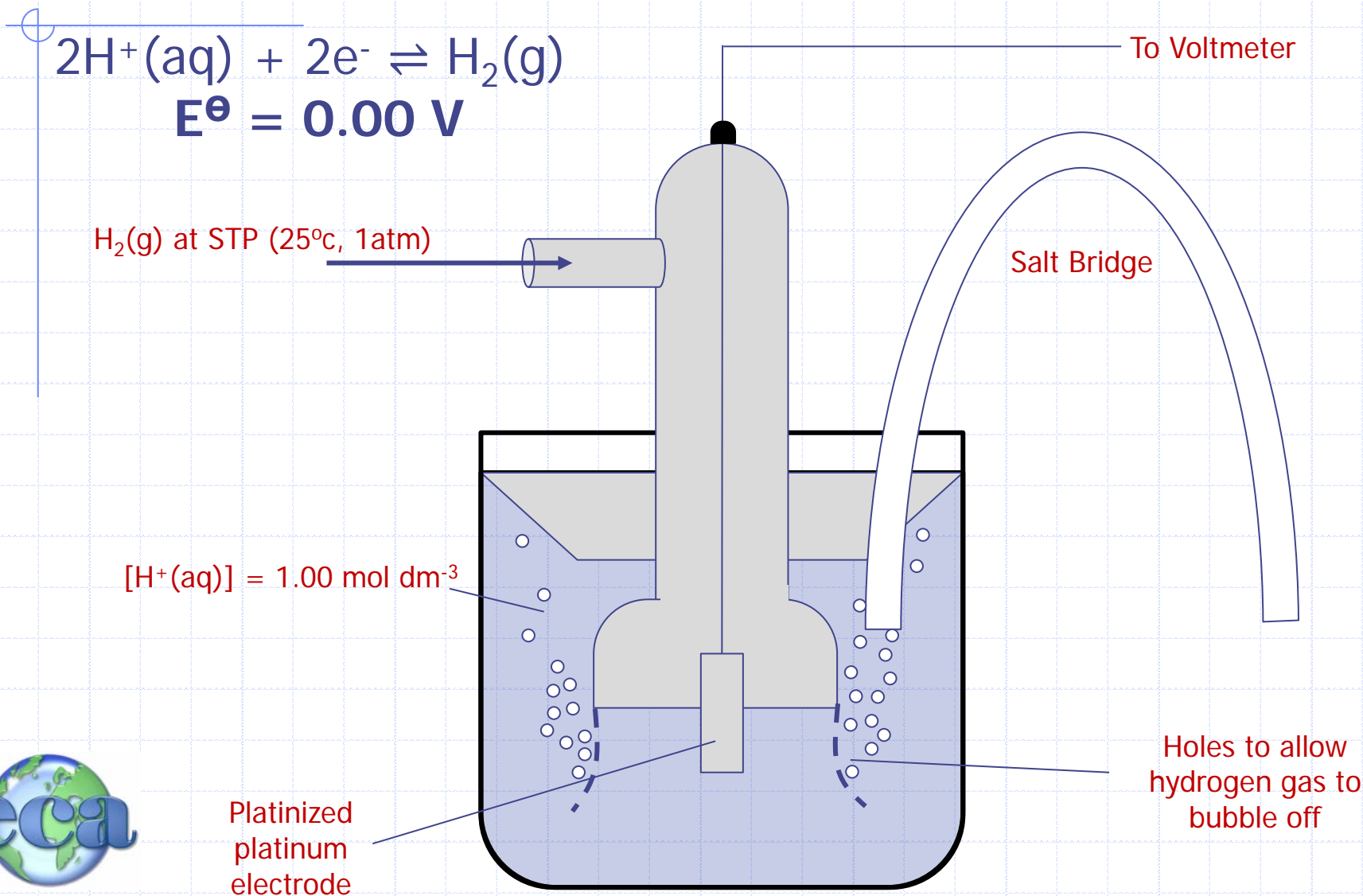
Difference in Potential Difference

- The **electrode potential** of an element depends only on:
 - The nature of the element (what it's made of)
 - The [concentration] of its ions in solution
 - The temperature of the solution
- For this reason, conditions of temp, [conc], and often pressure must be reported.
- Notice how the amount of metal present DOES NOT have an impact
- In order to measure the potential difference, there must be a standard to compare each to



The Standard Reference Electrode is the **Standard Hydrogen Electrode** which has $\text{H}_2(\text{g})$ in equilibrium with $\text{H}^+(\text{aq})$ ions.

Standard Hydrogen Electrode



Pt Electrode and Conditions

- The S.H.E. is maintained by a stream of pure $\text{H}_2(\text{g})$ bubbling over a Pt electrode immersed in a solution of HCl
- The Pt has these functions:
 - It acts as an inert metal connector to the $\text{H}_2(\text{g})/\text{H}^+(\text{aq})$ equilibrium. No tendency for the Pt electrode to ionize
 - The Pt surface acts as a catalyst and allows for potentials to be measured quickly.
 - An equilibrium between $\text{H}_2(\text{g})$ adsorbed on the electrode and the $\text{H}^+(\text{aq})$ in HCl solution
- Standard Conditions are:
 - Temperature of 298K (25°C)
 - Pressure of $\text{H}_2(\text{g})$ at 101,325 Pa (1 atm)
 - $[\text{H}^+(\text{aq})] = 1 \text{ mol dm}^{-3}$



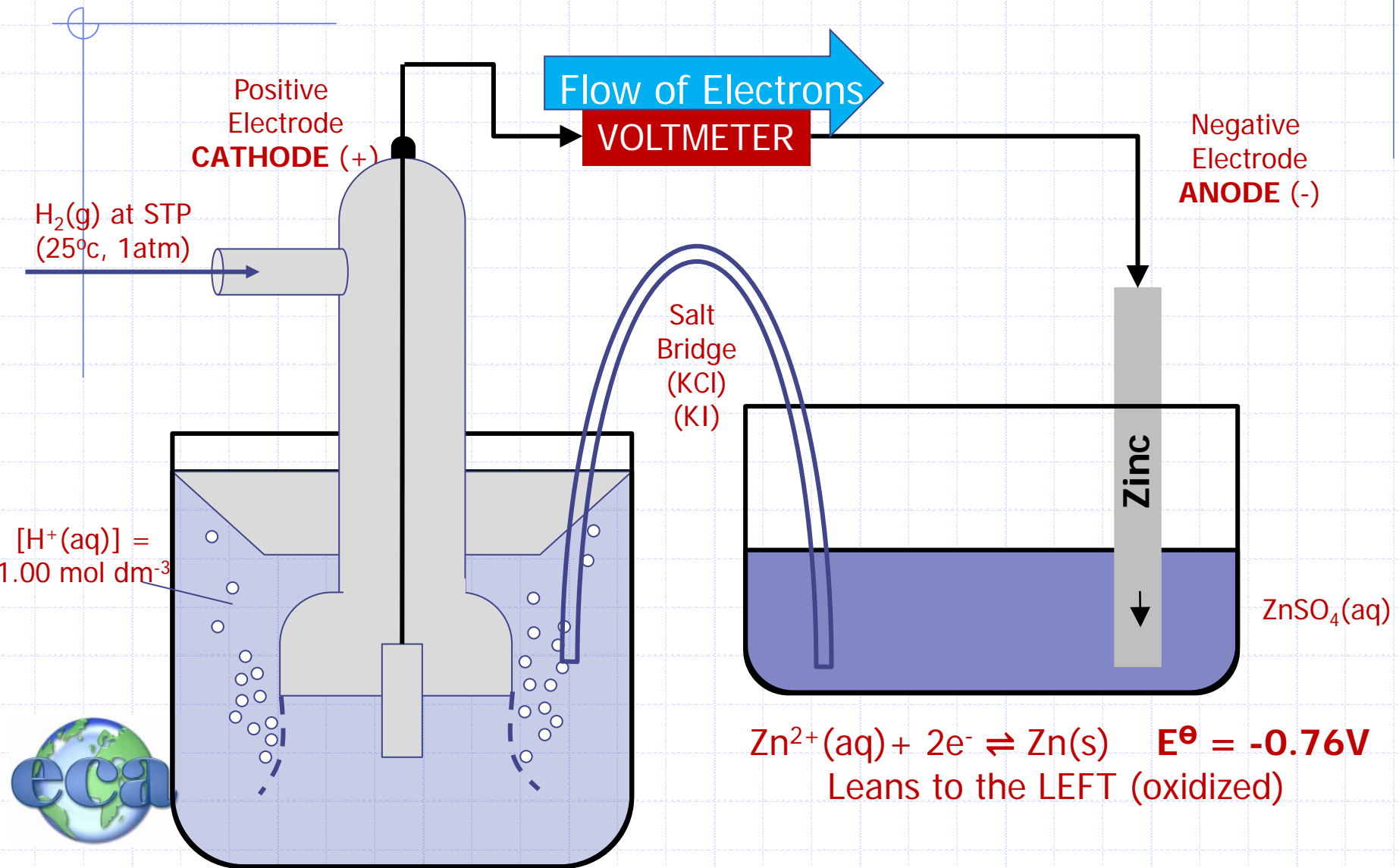
19.1 Definition of the Standard Electrode

19.1.2 Define the term standard electrode potential, E^\ominus . (1)

- The **standard electrode potential** is defined as the potential difference between a standard hydrogen electrode and a metal (the electrode) which is immersed in a $[1.0 \text{ mol dm}^{-3}]$ at 298 K and 1 atm
- This can be determined for any half-cell when hooked up with the standard hydrogen electrode (S.H.E.)
- If the result, E^\ominus , is:
 - **Negative ($E^\ominus < 0$)** – Electrode is oxidized when with S.H.E.
 - Ex: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$ $E^\ominus = -2.36 \text{ V}$
 - Powerful Reducing agents
 - **Positive ($E^\ominus > 0$)** – Electrode is reduced when with S.H.E.
 - Ex: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ $E^\ominus = +0.34 \text{ V}$
 - Powerful Oxidizing agents



Measuring Standard Electrode Potential of another metal half-cell



Cell Potentials

19.1.3 Calculate cell potentials using standard electrode potentials. (2)

- To calculate the cell potential, you must compare each of the half-cells
 - The half cell that is
 - Most negative (best reducing agent) will be oxidized
 - You will write the reverse reaction and flip the sign
 - For example, if lithium were oxidized:
 - $\text{Li}^+(\text{aq}) + 1\text{e}^- \rightleftharpoons \text{Li}(\text{s})$ $E^\ominus = -3.03 \text{ V}$ IN TABLE
 - $\text{Li}(\text{s}) \rightleftharpoons \text{Li}^+(\text{aq}) + 1\text{e}^-$ $E^\ominus = +3.03 \text{ V}$ FLIPPED FOR OXIDATION
 - Most positive (best oxidizing agent) will be reduced
 - You will keep the sign as is (+)
 - $\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s})$ $E^\ominus = -0.14 \text{ V}$ REDUCTION
 - Note that when the potentials of oxidation and reduction are added together, it's possible to have multiple combinations
 - $E^\ominus_{\text{oxidation}}(+1.0) + E^\ominus_{\text{reduction}}(+1.0) = E^\ominus_{\text{rxn}} = +2.0 \text{ V}$ (spontaneous)
 - $E^\ominus_{\text{oxidation}}(+1.0) + E^\ominus_{\text{reduction}}(-0.5) = E^\ominus_{\text{rxn}} = +0.5 \text{ V}$ (spontaneous)
 - $E^\ominus_{\text{oxidation}}(-0.5) + E^\ominus_{\text{reduction}}(-0.7) = E^\ominus_{\text{rxn}} = -0.2 \text{ V}$ (will not occur)



Cell Potential Calculation

■ Example with Magnesium and Ag:

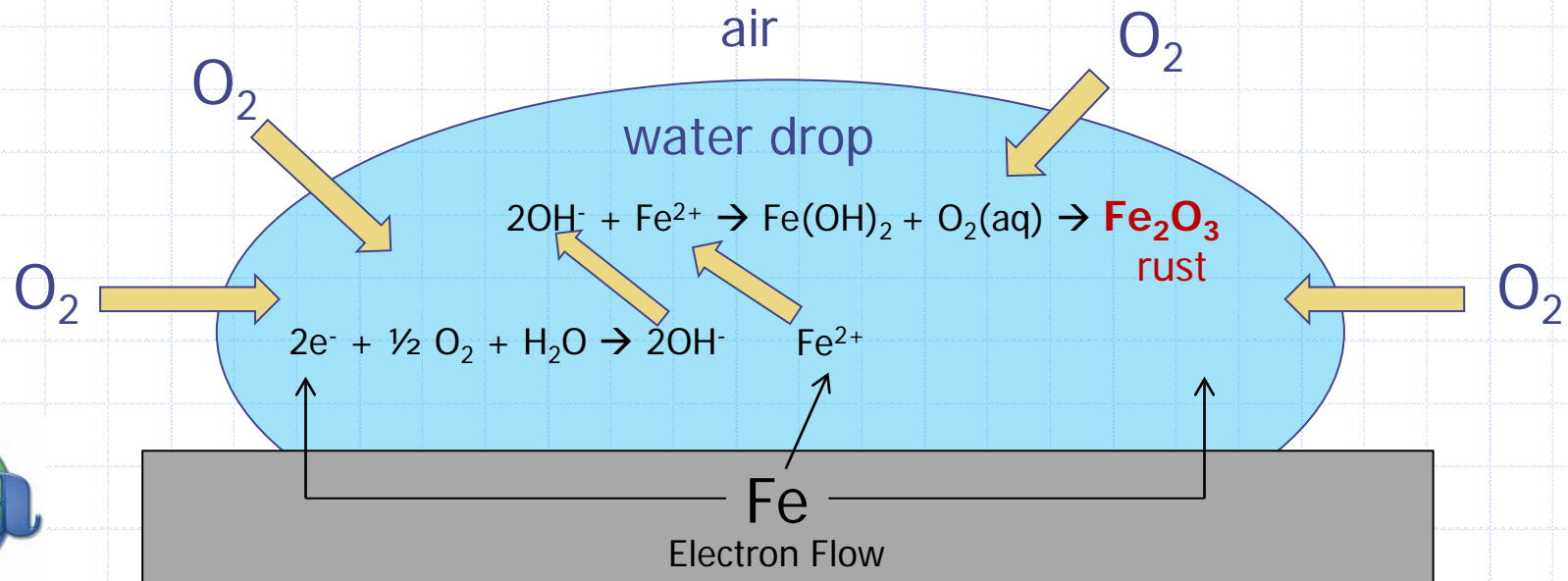
- $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Mg}(\text{s})$ $E^{\ominus} = -2.36 \text{ V}$
- $\text{Ag}^{+}(\text{aq}) + 1\text{e}^{-} \rightleftharpoons \text{Ag}(\text{s})$ $E^{\ominus} = +0.80 \text{ V}$
- $\text{Mg}(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{e}^{-}$ $E^{\ominus} = +2.36 \text{ V}$ OXIDIZED
- $\text{Ag}^{+}(\text{aq}) + 1\text{e}^{-} \rightleftharpoons \text{Ag}(\text{s})$ $E^{\ominus} = +0.80 \text{ V}$ REDUCED
- $\text{Mg}(\text{s}) + 2\text{Ag}^{+}(\text{aq}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$ $E^{\ominus} = +3.16 \text{ V}$ TOTAL
- Note how the degree of the potential does not change when the stoichiometric amount of Ag is doubled.
- The Cell diagram would be written as:
 - $\text{Mg}(\text{s})/\text{Mg}^{2+}(\text{aq})//\text{Ag}^{+}(\text{aq})/\text{Ag}(\text{s})$

- In order for a reaction to take place, and be spontaneous, it must result in a $E^{\ominus} > 0$ (positive)



Rusting of Iron

- In this process the simple oxidation is not very spontaneous
 - Reduction: Oxygen is reduced to OH^- ions
 - $\frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{OH}^- \quad E^\theta = +0.40 \text{ V}$
 - Oxidation: Iron is oxidized and Fe^{2+} ions pass into solution
 - $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \quad E^\theta = +0.44 \text{ V}$
 - Total:
 - $\frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{Fe}(\text{s}) \rightarrow 2\text{OH}^- + \text{Fe}^{2+}(\text{aq}) \quad E^\theta = +0.84 \text{ V}$
- Further oxidation turns Fe^{2+} into Fe^{3+} (rust)



19.1

Spontaneity of Reactions

19.1.4 Predict whether a reaction will be spontaneous using standard electrode potential values. (3)

- The maximum amount of electrical work that can be done by an electrochemical cell is equal to the Gibb's energy change (ΔG) with constant T&P.
 - $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$
 - n = electrons (in moles) transferred between electrodes
 - F = Faraday's constant ($96,485 \text{ C mol}^{-1}$) which is the amount of electrical charge carried by one mole of electrons
 - E^\ominus_{cell} = cell potential or voltage of the cell
- For $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
 - $n = 2 \text{ mol}$
 - $E^\ominus_{\text{cell}} = +1.10 \text{ V}$
 - $\Delta G^\ominus = (2)(96,485 \text{ C mol}^{-1})(1.10 \text{ V})$
 - $\Delta G^\ominus = -212 \text{ kJ mol}^{-1}$ (negative = spontaneous for GIBBS)



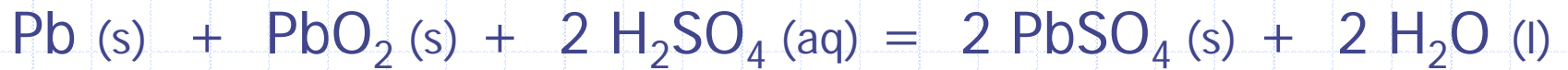
Batteries

- Batteries are Voltaic Cells
- Some can be recharged, others are dead when they no longer have a potential difference



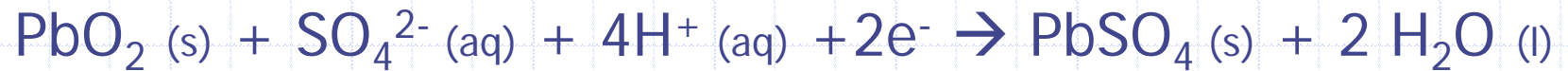
Lead-Acid (Car Battery)

Overall reaction

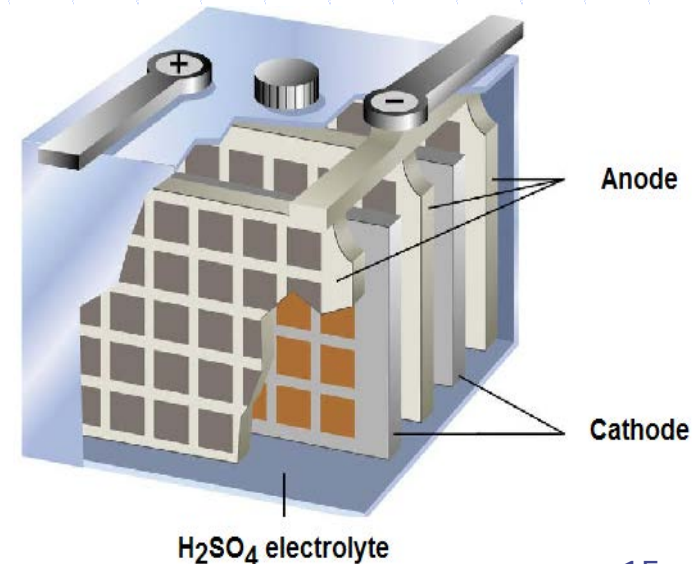


$E = 2.0$ - volts per cell

Cathode



Anode



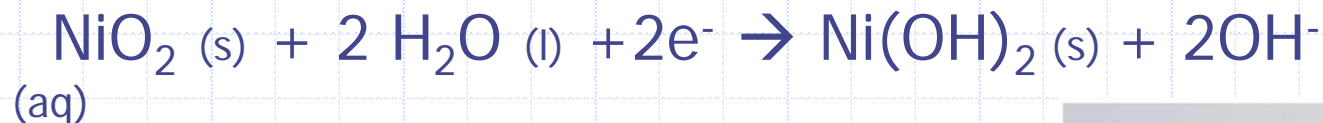
Nickel-Cadmium (Ni-Cad)

Overall reaction



$$E_{\text{NiCad}} = 1.25 \text{ v/cell}$$

Cathode



Anode

